Chiral Pyrimidine Metallacalixarenes: Synthesis, Structure and Host–Guest Chemistry

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Abstract: A set of enantiomerically pure cyclic multinuclear complexes with the formula *cis*-$[a_2PdL]_n^{n+}$ [a_2 = (*R*,*R*)-1,2-diaminocyclohexane (*R*,*R*-dach), (*S*,*S*)-1,2-diaminocyclohexane (*S*,*S*-dach); $n = 4$, 6; LH = 2-hydroxypyrimidine (2-Hpymo), 4,6-dimethyl-2-hydroxypyrimidine (2-Hdmpymo) and 4-hydroxypyrimidine (4-Hpymo)] were obtained by reaction of *cis*-$[a_2Pd(H_2O)_2]^{2+}$ and LH in aqueous media. The polynuclear complexes were studied by ^{1}H NMR spectroscopy and X-ray crystallography. These studies revealed that the *N*1,*N*3-bridging mode exhibited by the pyrimidine moieties is ideally suited for formation of inorganic analogues of calixarenes (metallacalixarenes) in a self-assembly process. The most stable species are the tetranuclear metallacalix[4]arenes, which are obtained in all cases. Hexanuclear species, namely, $[a_2Pd(2\text{-dmpymo})]_6^{6+}$, were also isolated and fully characterised. ^{1}H NMR experiments show conversion of $[a_2Pd(2\text{-dmpymo})]_6^{6+}$ to $[a_2Pd(2\text{-dmpymo})]_4^{4+}$ on heating. Analogously to organic calixarenes, these systems are also capable of incorporating hard metal ions at the oxo surface. Additionally, investigations on the receptor properties of these metallacalixarenes towards mononucleotides showed that enantioselective recognition processes occur in aqueous media.

Keywords: calixarenes · host–guest systems · molecular recognition · N,O ligands · palladium

Introduction

Transition-metal ions have been shown to be extremely important in self-assembly processes leading to discrete nanosized species or infinite coordination polymers.[1, 2] Small-protein-sized molecules have been synthesised in this way,[3] and there are numerous reports on exciting host–guest chemistry of such systems and interesting applications relevant to sensing and catalysis, among others.[2, 4] Molecular capsules have also been used to stabilise highly reactive species ("ship-in-a-bottle" synthetic strategies) and for carrying out selective reactions in the confined space of a capsule.[5, 6] In this context, implementation of chirality in these systems is of added value since it permits an entry to enantioselective processes, which are fundamental to many biological applications.[7]

Calixarenes, cyclic compounds possessing well-structured cavities, have been the subject of considerable attention due to their versatile behaviour as molecular receptors and ligands for metal ions.[8, 9] The interest in these systems has also drawn attention to the formation of coordination compounds analogous to calixarenes,[10] which considerably extend the properties of classic organic calixarenes as a result of the catalytic, spectroscopic and stereochemical properties intrinsic to metal ions.[3, 11]

A successful strategy for forming metallamacrocycles closely related to calix[*n*]arenes is the combination of a metal entity with 90° bond angles and an organic ligand providing 120° bond angles. This situation is ideally met by d^8 square-planar metal fragments and pyrimidine derivatives,[12] which respectively replace the methylene and phenol moieties of organic calixarenes.

Here we show how this strategy to build novel metallacalix[*n*]arenes easily allows us engineer their size and functionalisation by the appropriate choice of pyrimidine derivative and metal fragment. Thus, formation of metallacalix[*n*]arenes ($n = 4$, 6) is easily achieved by a self-assembly process involving *cis*-$[a_2Pd(H_2O)_2]^{2+}$ (a_2 = (*R*,*R*)-1,2-diaminocyclohexane (*R*,*R*-dach), *S*,*S*-1,2-diaminocyclohexane (*S*,*S*-dach)) metal fragments and simple hydroxypyrimidine derivatives (Scheme 1). This simple strategy offers a way of

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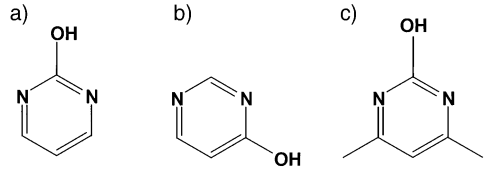


Scheme 1. a) 2-Hydroxypyrimidine (2-Hpymo), b) 4(3*H*)-pyrimidone (4-Hpymo), c) 4,6-dimethyl-2-hydroxypyrimidine (2-Hdmpymo).

controlling the size and functionalisation of the metallacalix[*n*]arene cavities, which results in a rich playground for host–guest chemistry. Furthermore, we can produce enantiomerically pure systems by means of *R*,*R*-dach or *S*,*S*-dach chelating ligands attached to the metal atoms.

We have also explored their behaviour as molecular hosts, for which their cationic and chiral nature makes them suitable as enantiospecific hosts for anionic guests. In this context, selective molecular recognition of DNA/RNA and their fragments is a key step in the development of selective catalysts for phosphodiester cleavage.[1a, 13] Thus, we also studied the host–guest chemistry of enantiomerically pure metallacalix[*n*]arenes with mononucleotides in aqueous media.

Results and Discussion

Synthesis: $[a_2PdL]_4(NO_3)_4$ (**1a**: $a_2 = R,R$-dach, LH = 2-hydroxypyrimidine (2-Hpymo); **1b**: $a_2 = S,S$-dach, LH = 2-Hpymo; **2a**: $a_2 = R,R$-dach, LH = 4,6-dimethyl-2-hydroxypyrimidine (2-Hdmpymo); **2b**: $a_2 = S,S$-dach, LH = 2-Hdmpymo; **4a**: $a_2 = R,R$-dach, LH = 4-hydroxypyrimidine (4-Hpymo); **4b**: $a_2 = S,S$-dach, LH = 4-Hpymo) were prepared by reaction of $[a_2Pd(H_2O)_2](NO_3)_2$ and LH in aqueous solution. $[a_2PdL]_6(NO_3)_6$ (**3a**: $a_2 = R,R$-dach, LH = 2-Hdmpymo; **3b**: $a_2 = S,S$-dach, LH = 2-Hdmpymo) were obtained from dilute solutions of **2a** and **2b**, respectively. Under these conditions, the corresponding $\mathbf{[a_2PdL]_n(NO_3)_n}$ compounds were isolated as suitable crystals for single-crystal X-ray diffraction after slow evaporation at room temperature. All compounds were characterised by elemental analyses, single-crystal X-ray diffraction and ^{1}H NMR spectroscopy. Additionally, recrystallisation of these complexes in presence of an excess of $La(NO_3)_3$ and $NaNO_3$ permitted isolation in the solid state of adducts of the types $\{La[(dach)PdL]_4\}(NO_3)_7$ (**1c** and **1d**) and $\{Na[(dach)PdL]_4\}(NO_3)_5$ (**1e** and **1f**) only for L = 2-pymo.

Crystal structures of 1b′, 1f, 2b, 3b and 4a: Suitable crystals for X-ray analysis were obtained for all compounds, but only crystals of **1b**, **1f**, **2b**, **3b** and **4a** were fully characterised by this technique. In the case of **1b**, the crystal selected for X-ray analyses was not representative of the sample, as it contained mononuclear $[(S,S\text{-dach})Pd(H_2O)_2]^{2+}$ in addition to tetranuclear $[(S,S\text{-dach})Pd(2\text{-pymo})]_4(NO_3)_4$ (see below). For this reason, we denote this compound as **1b′**.

A selection of crystal and structure refinement parameters for these compounds is summarised in Table 1. All these systems crystallise in noncentrosymetric space groups, which is consistent with their chiral nature.

Compounds **1b′**, **1f**, **2b** and **4a** consist of tetranuclear cyclic $[(dach)Pd(pymo\text{-}N1,N3)]_4^{4+}$ (**1b′**, *S*,*S*-dach, 2-Hpymo; **1f**, *S*,*S*-dach, 2-Hpymo; **2b**, *S*,*S*-dach, 2-Hdmpymo; **4a**, *R*,*R*-dach, 4-Hpymo) cations, nitrate counterions and water molecules of hydration.

Perspective views of cations $[(R,R\text{-dach})Pd(2\text{-pymo-}N1,N3)]_4^{4+}$, $[(S,S\text{-dach})Pd(2\text{-dmpymo-}N1,N3)]_4^{4+}$ and $[(R,R\text{-dach})Pd(4\text{-pymo-}N1,N3)]_4^{4+}$ are depicted in Figure 1a, b and

Table 1. Crystallographic data for **1b′**, **1f**, **2b**, **3b** and **4a**.

Compound	**1b′**	**1f**	**2b**	**3b**	**4a**
Empirical formula	$Pd_5C_{46}H_{114}N_{24}O_{38}$	$Pd_4C_{40}H_{88}N_{21}O_{29}Na$	$Pd_4C_{48}H_{104}N_{20}O_{26}$	$Pd_6C_{72}H_{186}N_{30}O_{54}$	$Pd_4C_{40}H_{92}N_{20}O_{28}$
M_r	2143.64	1775.93	1803.15	2974.96	1726.97
crystal system	monoclinic	orthorhombic	cubic	monoclinic	triclinic
space group	*C*2	$C222_1$	$P2_13$	$P2_1$	*P*1
a [Å]	35.08(7)	32.38(5)	36.727(3)	18.324(4)	13.869(3)
b [Å]	9.37(2)	35.77(5)	36.727(3)	14.291(3)	15.533(3)
c [Å]	29.72(6)	30.43(4)	36.727(3)	23.343(3)	18.033(4)
α [°]	90	90	90	90	111.46(3)
β [°]	91.28(3)	90	90	95.71(3)	103.65(3)
γ [°]	90	90	90	90	92.95(3)
V [Å^3]	9769	35242	49571	6082	3472
Z	16	16	24	2	2
ρ_{calcd} [Mg/m^{-3}]	1.43	1.32	1.45	1.39	1.65
$\mu(Mo_{K\alpha})$ [mm^{-1}]	0.98	0.88	0.93	0.94	1.11
T [K]	293(2)	293(2)	173(2)	293(2)	293(2)
crystal size [mm]	0.25 × 0.15 × 0.10	0.32 × 0.27 × 0.20	0.36 × 0.25 × 0.21	0.25 × 0.20 × 0.15	0.30 × 0.25 × 0.20
$2\theta_{max}$ [°]	54	56	50	56	56
reflns. collected	20581	200435	505553	23261	15633
independent rflns.	11315	41024	29186	23261	15633
reflns. obsd	4562	31662	24101	10855	6931
parameters refined	787	1413	1437	1244	700
R_1[a]	0.083	0.119	0.077	0.048	0.098
wR_2[b]	0.27	0.34	0.224	0.114	0.314
goodness of fit	0.879	1.279	1.053	0.827	1.023
residuals [e Å^{-3}]	1.22/ – 1.20	2.060/ – 2.055	1.590/ – 0.700	0.940/ – 0.420	1.476/ – 1.253

[a] $R_1 = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

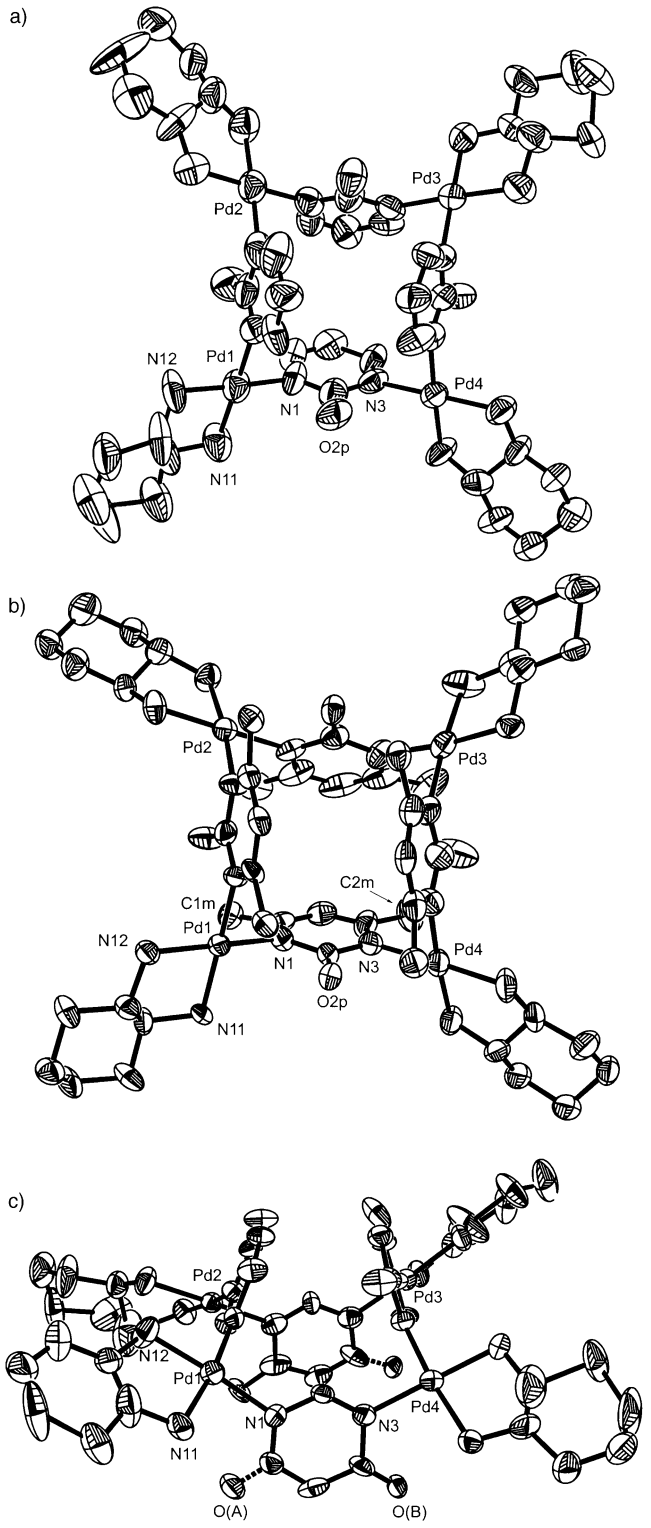


Figure 1. a) Perspective view of the cation $[(dach)Pd(2\text{-}pymo)]_4^{4+}$ in the crystal structure of **1b′**. b) Perspective view of the cation $[(dach)Pd(2\text{-}dmpymo)]_4^{4+}$ in the crystal structure of **2b**. c) View of the cation $[(dach)Pd(4\text{-}pymo)]_4^{4+}$ in the crystal structure of **4a**. Disorder in **4a** prevented unequivocal location of the exocyclic oxygen atoms of pyrimidine moieties, which can be located in position A or B in each pyrimidine ring.

c, respectively. X-ray analyses show that, regardless of pyrimidine functionalisation, an *N*1,*N*3-bridging mode is present in all cases and leads to a metallacalix[4]arene. In **1b′** and **1f**, the four Pd centres lie on a nearly perfect square plane, whereas in **2b** and **4a** the Pd atoms form a square folded along the diagonal with a dihedral angle of about 14° (Table 2). In all cases, the square sides measure about 5.8 Å.

Table 2. Selected average bond lengths [Å] and angles [°] for **1b′**, **1f**, **2b**, **3b** and **4a**.

	1b′	**1f**	**2b**	**3b**	**4a**
Pd···Pd′	5.83(1)	5.80(1)	5.77(1)	5.77(1)	5.82(1)
Pd–N(pymo)	2.05(1)	2.03(1)	2.04(1)	2.05(1)	2.05(1)
Pd–N(dach)	2.07(1)	2.02(1)	2.04(1)	2.05(1)	2.05(1)
Na–O		2.21(1)			
N(pymo)-Pd-N(pymo)	88.4(4)	89.5(4)	91.4(4)	94.0(3)	92.7(4)
N(dach)-Pd-N(dach)	84.3(4)	84.3(4)	84.1(4)	83.2(3)	84.5(5)
N(dach)-Pd-N(pymo)	93.7(5)	93.1(3)	91.2(5)	91.4(3)	91.4(5)

The geometry of the pyrimidine moieties is similar to that found in other compounds containing related ligands exhibiting the same bridging coordination mode.[14] In all cases, the pyrimidine rings are not coplanar with the Pd_4 plane and display a 1,3-alternating arrangement similar to that previously found in $[(en)Pt(uracilate)]_4(NO_3)_4$[10] and $[(en)M(2\text{-}pymo)]_4(NO_3)_4$[15] metallacalix[4]arenes. As expected, the dach ligands are responsible for the homochiral nature of the cyclic cations.

For compound **4a**, significant disorder prevents unequivocal location of the exocyclic oxygen atoms of the pyrimidine moieties (see Figure 1c). This disorder is due to the asymmetry of the 4-Hpymo ligand, which leads to formation of several species in which the oxygen atoms can be located in position A or B in each pyrimidine ring (see Figure 1c).

The crystal structure of **1f** is an interesting example of the ability of metallacalix[*n*]arenes to interact with additional metal ions.[16] In this case, the overall features of tetranuclear cations $[(S,S\text{-}dach)Pd(2\text{-}pymo)]_4^{4+}$, such as 1,3-alternating conformation, are maintained (Figure 2). Additionally, two

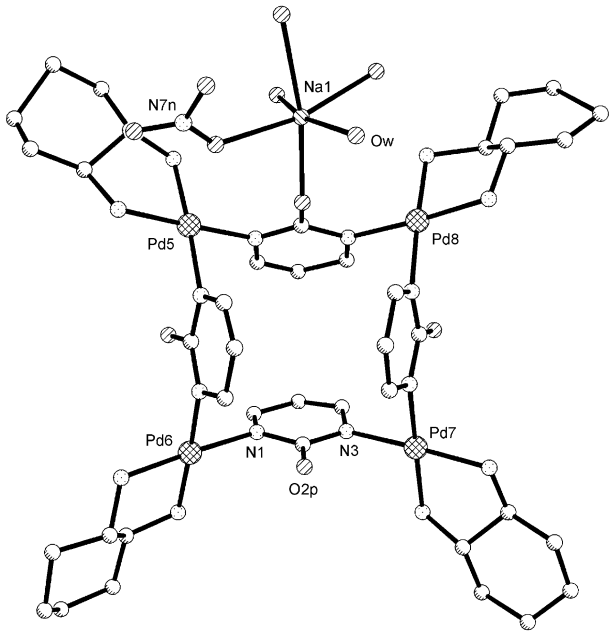


Figure 2. View of the structure of **1f**. The cation $[(dach)Pd(2\text{-}pymo)]_4^{4+}$ with an Na ion coordinated to the exocyclic oxygen atom of a pyrimidine moiety is depicted.

hydrated Na ions are found in the asymmetric unit composed of two crystallographically independent tetranuclear $[(S,S\text{-dach})Pd(2\text{-pymo})]_4^{4+}$ cations. Nevertheless, only one of the two alkali metal ions directly interacts with a metallacalix[4]-arene. This interaction occurs between the alkali metal ion and one exocyclic pyrimidine oxygen atom. This is consistent with the weakness of alkali metal–metallacalix[4]arene interactions, which are not observed in solution (see below).

In contrast to the above complexes, compound **3b** contains hexanuclear cyclic $[(S,S\text{-dach})Pd(2\text{-dmpymo-}N1,N3)]_6^{6+}$ ions. A view of the structure of **3b** is shown in Figure 3. As expected, Pd binding occurs at the N1 and N3 donor atoms of the pyrimidine ring. In this case, the six Pd centres lie on a plane (mean deviation of ca. 0.01 Å) generating a distorted hexagon 8.2 Å wide and 13.9 Å long. The folding of the molecule can be explained in terms of hydrophobic interactions between the methyl groups and the π electrons of the pyrimidine moieties, which are separated by about 3.2 Å. This novel geometry is also responsible for a separation of adjacent Pd centres similar to that found in previous tetranuclear species (Table 2).[10] Analogous to the above-mentioned metallacalix[4]arenes, the pyrimidine rings are not coplanar with the Pd_6 plane and show a 1,3,5-alternating arrangement.

^{1}H NMR studies: ^{1}H NMR studies on these compounds (Table 3) show the complex effect of pyrimidine functionalisation on the process of metallacalix[*n*]arene formation. Thus, in the 1:1 reaction between $[(dach)Pd(H_2O)_2]^{2+}$ (enantiomerically pure $[(R,R\text{-dach})Pd(H_2O)_2]^{2+}$ or $[(S,S\text{-dach})Pd(H_2O)_2]^{2+}$) and symmetric 2-Hpymo in aqueous media, quantitative formation of a single species **1** (**1a** or **1b**) is observed. However, if 2-Hdmpymo is used instead of 2-Hpymo, this reaction leads to the formation of two cyclic species **2** and **3** (**2a** or **2b** and **3a** or **3b**, respectively). Fresh solutions of compounds **2b** and **3b** gave the same spectrum as **2** and **3**, respectively. Finally, in the case of an asymmetric 4-Hpymo ligand, the analogous reaction is further complicated, and several tetranuclear species are generated (see below).

The ^{1}H NMR spectra of all compounds isolated are indicative of a *N*1,*N*3-bridging coordination mode of the pyrimidine ligands. Thus, replacement of acidic protons at the endocyclic basic nitrogen atoms in $2\text{-}H_2pymo^+$ is responsible for a significant high-field shift of the aromatic protons of 2-pymo. The chirality of the auxiliary ligand provokes the loss of the original equivalence of the two halves of the aromatic ring, and two signals then appear for H4 (Table 3).

In the case of $2\text{-}H_2dmpymo^+$, two different species are generated. Tetranuclear **2** species show a high-field shift of the H5 resonance and a downfield shift and concomitant loss of the original equivalence of methyl groups. In the case of **3**, a larger high-field shift of H5 and slight downfield shifts of methyl resonances are observed. The large downfield shift for the methyl groups[17] in **2** is a consequence of their location over the metal coordination plane when a square-planar d^8 metal center[18] binds to the endocyclic nitrogen atoms of 2-dmpymo. This observation could also be indicative of a weak M···H interac-

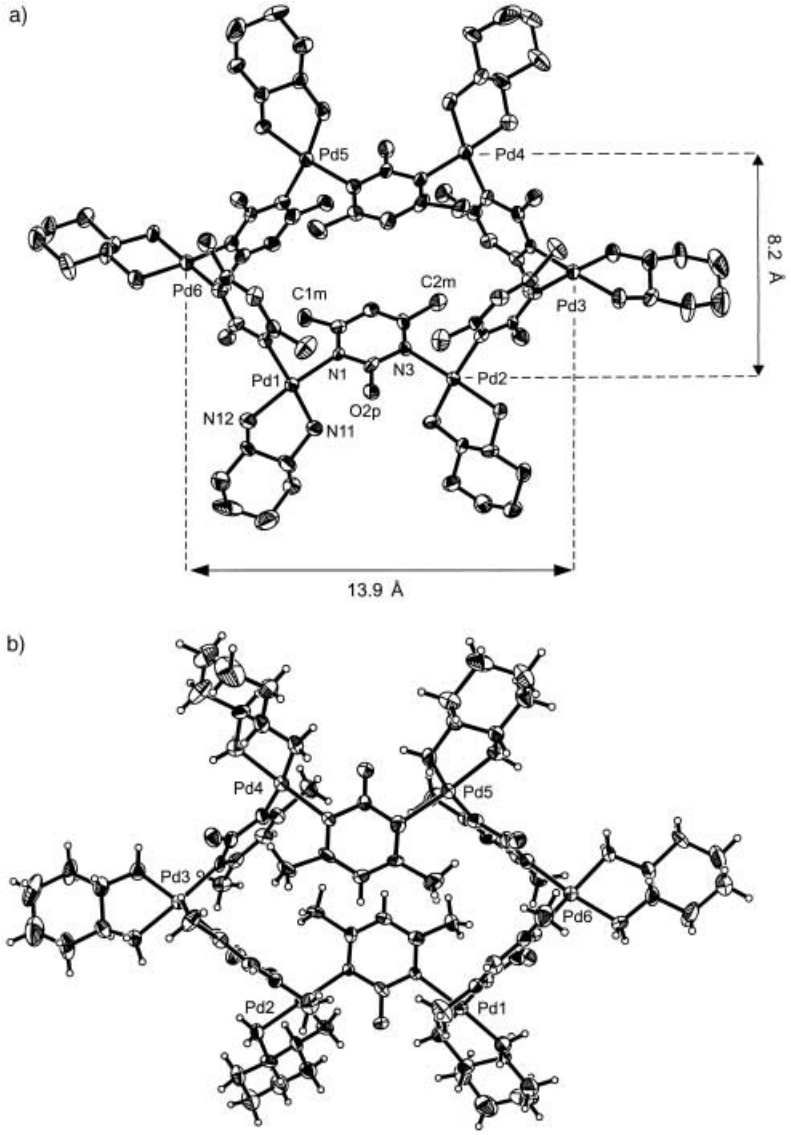


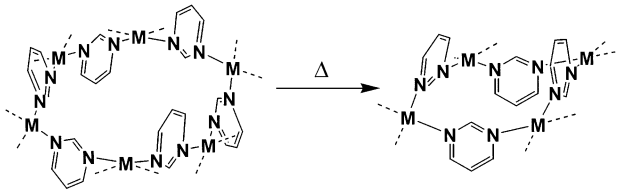
Figure 3. Two perspective views of the cation $[(dach)Pd(2\text{-dmpymo})]_6^{6+}$ in the crystal structure of **3b**. Folding of the molecule due to hydrophobic interactions between the methyl groups and the π electrons of the pyrimidine moieties is evident (b).

Table 3. ^{1}H NMR (200 MHz) chemical shifts [ppm] in the aromatic region and coupling constants [Hz] for compounds **1a**, **1b**, **2a**, **2b**, **3a**, **3b**, **4a**, **4b** and **5** (D_2O at 295 K, pH* 6).

Compound	H2	H4, H4	H5	H6	Me, Me′
2-Hpymo · HCl		8.72 ($J_{4,5}=5.9$)	7.05 ($J=5.9$)		
2-Hdmpymo · HCl			6.77		2.58
4-Hpymo · HCl	9.26		6.81 ($J_{5,6}=6.9$)	8.09 ($J=6.9$)	
1a, 1b		8.20, 8.30 ($J_{4,5}=5.6$, $J_{4,4'}=2.7$)	6.47 ($J=5.6$)		
2a, 2b			6.31		3.00, 3.13
3a, 3b			6.18		2.61, 2.65
4a, 4b	8.12, 8.15, 8.25, 8.27, 8.28, 8.32, 8.40, 8.47		6.25, 6.28, 6.31	7.90	
5	8.36		6.53 ($J_{5,6}=6.9$)	8.02 ($J=6.9$)	

tion[19] (M···H separation of ca. 2.6 Å), which can be described as a three-centre, four-electron M···H–C interaction,[20] in contrast to the classical three-centre, two-electron agostic interactions. For **3**, the lower downfield shifts of the methyl resonances can be explained by the disposition of methyl groups over the pyrimidine rings (separation of methyl and pyrimidine plane is ca. 3.2 Å). This situation implies significant shielding of the methyl groups because of the π orbitals of the pyrimidine ligand, which counteracts the anisotropic effect of M···H–C interactions, which are also present in this case.

The presence of a single set of resonances in **1**, **2** and **3** for the pyrimidine signals indicates the equivalence of all aromatic moieties in solution. Indeed, variable-temperature experiments (up to 70 °C in D_2O; −50 °C in MeOD) did not indicate any change in the basic features of the spectra, in agreement with highly conformationally flexible metallacalix[*n*]arenes. In the case of **3**, experiments at higher temperatures showed slow conversion of hexanuclear **3** cations into the entropically favoured tetranuclear complexes **2** (Scheme 2). This process is complete after heating at 60 °C

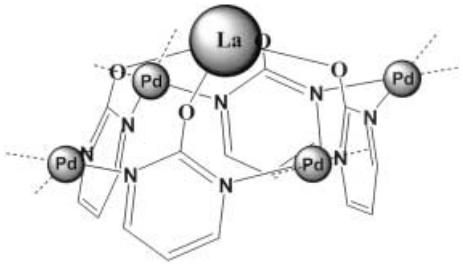


Scheme 2. Conversion of metallacalix[6]arene to metallacalix[4]arene.

for about 6 h; however, at room temperature, there is no appreciable change in the ^{1}H NMR resonances with time. Nevertheless, if crystallisation takes place from dilute solutions, the hexanuclear species **3** are isolated in the solid state as main products. This behaviour can be related to a concentration dependence similar to that found by Fujita et al. for tetrameric and a trimeric cyclic systems.[21] We are aware that other factors can also influence the distribution.[22]

Another characteristic feature of the NMR spectra of **1, 2** and **3** is the loss of the original equivalence of the two halves of the pyrimidine moieties as a consequence of the asymmetry introduced by the dach ligands at the metal centres (Table 3).

The presence of exocyclic oxygen atoms at the pyrimidine moieties prompted us to explore their behaviour as ligands for hard metal ions. Thus, addition of lanthanum salts to aqueous solutions of **1, 2, 3** and **4** does not have any effect on the ^{1}H NMR spectra, which rules against any appreciable interaction between the La^{III} ions and the oxo surface of the metallacalixarenes in polar solvents such as water and methanol. However, when lanthanum salts were added to solutions containing **1a** or **1b, 1c** and **1d**, adducts (Scheme 3)



Scheme 3. Proposed structure for **1c** and **1d**.

were obtained as solids in good yields, and this implies a conformational change from 1,3-alternating to a cone conformation on binding lanthanum. In contrast, neither **2** nor **3** give any adduct with La^{III} in the solid state, which may be related to their alternating orientation of the exocyclic oxygen atoms and the sterically hindered rotation about the Pd–N bonds due to the bulky methyl substituents and diaminocyclohexane. This fact may explain the low yield obtained in the synthesis of related $\{Gd[(en)Pd(2\text{-}dmpymo)]_4\}(NO_3)_7$.[23] Additionally, the capability of the exocyclic pyrimidine oxygen atoms to coordinate metal ions is confirmed in the crystal structure of **1f**, which shows an interaction with a sodium cation. In contrast to lanthanum adducts, interaction with sodium does not imply any conformational change to a cone conformation.

In the case of the asymmetric ligand 4-Hpymo, the observation of several sets of signals indicates the generation of different species. As discussed above, these are also present in a single crystal. The first set of resonances of aromatic protons, in the range $\delta = 6.20 - 6.38$ ppm, belongs to H5 protons (Table 3). H6 appears as a broad signal in the $\delta = 7.76 - 8.05$ ppm region, whereas for H2 eight signals between $\delta = 8.11$ and 8.50 ppm are observed. This is explained by the different possibilities for the relative orientation of the exocyclic oxygen atoms of the pyrimidine moieties in **4**.

We simplified this situation by performing the same reaction on an NMR scale with ethylenediamine instead of

1,2-diaminocyclohexane as blocking ligand. In this case, a single species **5** is observed in the ^{1}H NMR studies.

These results show the effect of the asymmetry and the steric hindrance introduced by exocyclic substituents on dach in the complexes. In this regard, the possibility of isolating two species should be noted, namely metallacalix[6]arene **3** and metallacalix[4]arene **2**, as well as formation of multiple species in the case of metallacalix[4]arenes containing 4-pymo.

Host–guest chemistry: The cationic and chiral nature of these systems prompted us to study their host–guest chemistry towards biologically relevant anionic guests. The properties of these materials as molecular receptors of mononucleotides were investigated in aqueous solution by means of ^{1}H NMR spectroscopy. The experiments show that significant molecular recognition processes only take place between metallacalix[4]arenes **2a** and **2b** and adenosine 5′-monophosphate (AMP). Guanosine 5′-monophosphate (GMP), thymidine 5′-monophosphate (TMP) and cytidine 5′-monophosphate (CMP) are not recognised, which points to a significant contribution of hydrophobic interactions in the recognition process.[24]

The ^{1}H NMR experiments clearly show the enantioselective nature of supramolecular interactions between **2** and AMP. Figure 4 shows the effect of adding AMP to a solution containing [(*R*,*R*-dach)Pd(2-dmpymo)]$_4$(NO$_3$)$_4$ and [(*S*,*S*-dach)Pd(2-dmpymo)]$_4$(NO$_3$)$_4$ enantiomers (1:1 ratio) on the ^{1}H NMR spectra. These experiments showed that addition of an excess of AMP (1:4 ratio) splits the H5 signals of the metallacalix[4]arene (Figure 4b). The resulting high-field shifts of the H5 protons of the metallacalix[4]arenes and the downfield shifts of the AMP H8 and H2 protons is attributable to a supramolecular interaction. The observed shifts are $\Delta\delta = -0.05$ and -0.04 for the H5 resonances of the *R*,*R* and *S*,*S* isomers, respectively. The H8 and H2 AMP resonances are shifted by $\Delta\delta = +0.03$ and $+0.01$, respectively. The splitting of the metallacalix[4]arene H5 signals is due to the slightly different affinities of the *R*,*R* and *S*,*S* enantiomers for AMP (the relatively small enantiomeric effect can be related to the separation between the recognition site and the chiral centres).

Addition of a larger quantity of the *R*,*R* isomer permits unequivocal assignment of the respective diasteroisomers (Figure 4c).

In contrast to **2a** and **2b**, closely related **1a** and **1b** do not show any significant supramolecular interactions with AMP. We attribute this different behaviour to a change in size and polarity of the cavity of **2a** and **2b** as a consequence of the methyl substituents. This closely resembles the host–guest chemistry of classical calix[*n*]arenes, for which rings substituted on the upper rim (e.g., with *tert*-butyl groups) have richer receptor properties than unsubstituted rings.[8] Interestingly, these interactions also do not take place with metallacalix[6]arenes [(*R*,*R* or *S*,*S*-dach)Pd(2-dmpymo)]$_6$(NO$_3$)$_6$], despite the fact that they are assumed to have wider cavities. This fact can be explained by the folding of the molecule due to hydrophobic intramolecular interactions between the methyl groups and the π electrons of the pyrimidine moieties (see above).

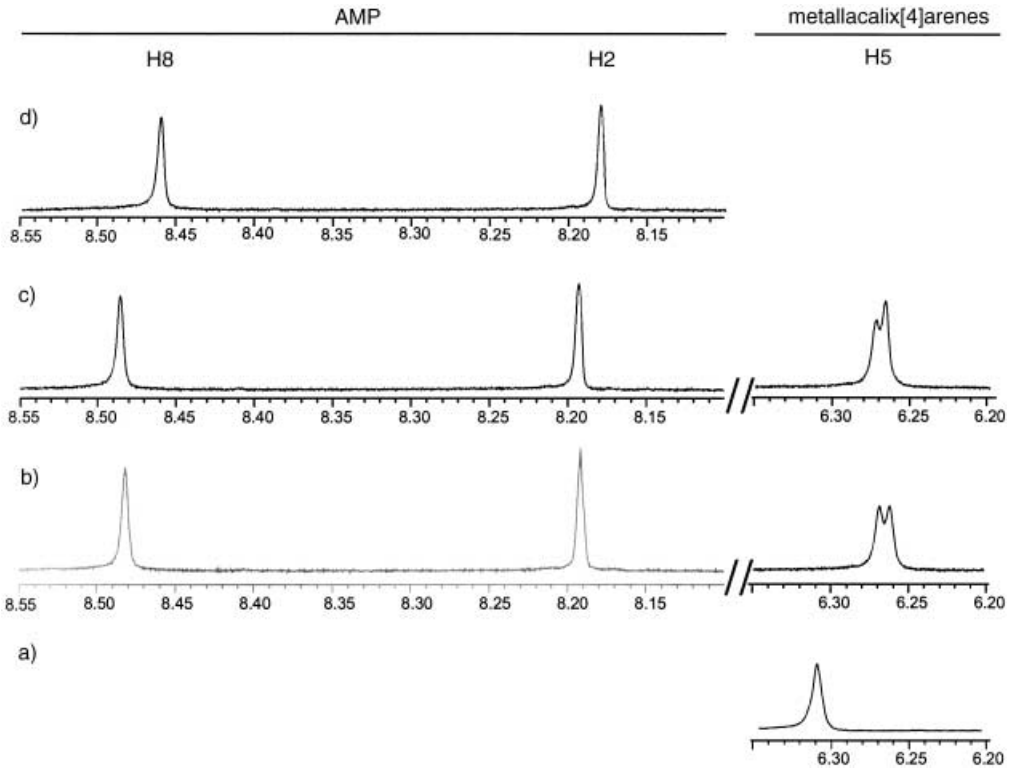


Figure 4. a) H5 signal for a solution containing [(*R*,*R*-dach)Pd(2-dmpymo)]$_4$(NO$_3$)$_4$ and [(*S*,*S*-dach)Pd(2-dmpymo)]$_4$(NO$_3$)$_4$ enantiomers (1:1 ratio). b) Splitting of metallacalix[4]arene H5 signal due to the addition of AMP (1:4 ratio). c) Addition of a larger quantity of the *R*,*R*-isomer permits unequivocal assignment of the respective diasteroisomers. d) H8 and H2 signals of free AMP (pH* 6).

In all cases, AMP induces decomposition of the cyclic structure of the metallacalix[*n*]arenes over several hours to give complexes of the type [(*R*,*R* or *S*,*S*-dach)Pd(AMP)$_2$]. Analogous processes are also observed with the other mononucleotides.

Conclusion

Enantiomerically pure cyclic polynuclear complexes with different nuclearities have been synthesised. The tetranuclear species are clearly thermodynamically favoured, which can be explained by considering entropic reasons. This is similar to organic calixarenes, for which calix[4]arenes are also the most favoured species.

The recognition of mononucleotides by metallacalixarenes followed by cross-linking reactions may open the possibilities of employing metallacalixarenes as selective metal-based DNA-binding drugs.

Experimental Section

Materials and methods: 2-Hydroxypyrimidine·HCl (2-Hpymo·HCl), (1*R*,2*R*)-1,2-diaminocyclohexane·L-tartaric acid (*R*,*R*-dach·L-tartaric acid) and (1*S*,2*S*)-1,2-diaminocyclohexane·D-tartaric acid (*S*,*S*-dach·D-tartaric acid purchased from Aldrich, were converted to the corresponding HNO_3 adducts by anion exchange. 4,6-Dimethyl-2-hydroxypyrimidine (2-Hdmpymo), 4(3*H*)-pyrimidone (4-Hpymo), and monosodium salts of adenosine 5′-monophosphate (AMP), thymidine 5′-monophosphate (TMP), cytidine 5′-monophosphate (CMP) and guanosine 5′-monophosphate (GMP) were used as received (Aldrich). Potassium tetrachloropalladate was supplied by Johnson Matthey. [(en)PdCl$_2$], [(*R*,*R*-dach)PdCl$_2$] and [(*S*,*S*-dach)PdCl$_2$] were prepared by standard methods.[25]

Synthesis of [a$_2$PdL]$_4$(NO$_3$)$_4$ (1a: a$_2$ = *R*,*R*-dach, LH = 2-Hpymo; 1b: a$_2$ = *S*,*S*-dach, LH = 2-Hpymo; 2a: a$_2$ = *R*,*R*-dach, LH = 2-Hdmpymo; 2b: a$_2$ = *S*,*S*-dach, LH = 2-Hdmpymo; 4a: a$_2$ = *R*,*R*-dach, LH = 4-Hpymo; 4b: a$_2$ = *S*,*S*-dach, LH = 4-Hpymo): [a$_2$PdCl$_2$] (4 mmol) was added to an aqueous solution of $AgNO_3$ (1.36 g, 8 mmol) in water (30 mL), and the suspension was stirred in the dark at 40 °C overnight. The resulting mixture was kept at 4 °C for 1 h before the AgCl precipitate was filtered off. A solution of LH in water (4 mmol in 20 mL) was added to the filtrate and, after raising the pH to 5.5 by means of 1M NaOH, the mixture was allowed to react at 60 °C for 6 h. Subsequent concentration of the solution to 15 mL by rotary evaporation gave the corresponding [a$_2$PdL]$_4$(NO$_3$)$_4$ compounds after seven days at room temperature.

[(dach)Pd(2-pymo)]$_4$(NO$_3$)$_4$·*n*H$_2$O (*n* = 14; *R*,*R*: 1a, *S*,*S*: 1b): Elemental analysis (%) calcd for $Pd_4C_{40}H_{96}N_{20}O_{30}$ (1763.00): C 27.25, H 5.49, N 15.73; found: C 27.28, H 5.77, N 15.57. Yield 53%. ^{1}H NMR (200 MHz, D_2O, 25 °C, TMA): $\delta = 1.01-1.43$ (m, 4H; dach), 1.53–1.75 (m, 2H; dach), 1.89–2.10 (m, 2H; dach), 2.49–2.70 (m, 2H; dach), 6.47 (t, $J_{5,4} = J_{5,4'} = 5.6$ Hz, 1H; H_5), 8.20 (dd, $J_{4,4'} = 2.7$ Hz, 1H; H_4), 8.30 ppm (dd, 1H; $H_{4'}$).

[(dach)Pd(2-dmpymo)]$_4$(NO$_3$)$_4$·*n*H$_2$O (*n* = 10; *R*,*R*: 2a, *S*,*S*: 2b): Elemental analysis (%) calcd for $Pd_4C_{48}H_{104}N_{20}O_{26}$ (1803.15): C 31.97, H 5.81, N 15.54; found: C 31.86, H 6.19, N 15.68. Yield 50%. ^{1}H NMR (200 MHz, D_2O, 25 °C, TMA): $\delta = 1.01-1.43$ (m, 4H; dach), 1.53–1.75 (m, 2H; dach), 1.89–2.10 (m, 2H; dach), 2.49–2.70 (m, 2H; dach), 3.00 (s, 3H; Me), 3.13 (s, 3H; Me′), 6.31 ppm (s, 1H; H_5).

[(dach)Pd(4-pymo)]$_4$(NO$_3$)$_4$·*n*H$_2$O (*n* = 12; *R*,*R*: 4a, *S*,*S*: 4b): Elemental analysis (%) calcd for $Pd_4C_{40}H_{92}N_{20}O_{28}$ (1726.97): C 27.82, H 5.37, N 16.22; found: C 27.88, H 5.89, N 16.62. Yield 53%. ^{1}H NMR (200 MHz, D_2O, 25 °C, TMA): $\delta = 1.01-1.43$ (m, 4H; dach), 1.53–1.75 (m, 2H; dach), 1.89–2.10 (m, 2H; dach), 2.49–2.70 (m, 2H; dach), 6.28 (br, 1H; H_5), 7.90 (br, 1H; H_6), 8.32 ppm (1H; H_2).

Synthesis of [a$_2$PdL]$_6$(NO$_3$)$_6$ (3a: a$_2$ = *R*,*R*-dach, LH: 2-Hdmpymo; 3b: a$_2$ = *S*,*S*-dach, LH = 2-Hdmpymo): These compounds were prepared by following the above-described procedure, except that the concentration process was omitted. These conditions permit the isolation of [a$_2$PdL]$_6$(NO$_3$)$_6$ after four days at room temperature.

[(dach)Pd(2-dmpymo)]$_6$(NO$_3$)$_6$·*n*H$_2$O (*n* = 30; *R*,*R*: 3a, *S*,*S*: 3b): Elemental analysis (%) calcd for $Pd_6C_{72}H_{186}N_{30}O_{54}$ (2974.96): C 29.07, H 6.30, N 14.12; found: C 29.19, H 6.56, N 14.32. Yield 15%. ^{1}H NMR (200 MHz, D_2O, 25 °C, TMA): $\delta = 1.01-1.43$ (m, 4H; dach), 1.53–1.75 (m, 2H; dach), 1.89–2.10 (m, 2H; dach), 2.61 (s, 3H; Me), 2.65 (s, 3H; Me′), 6.18 ppm (s, 1H; H_5).

Synthesis of {La[(dach)Pd(2-pymo)]$_4$}(NO$_3$)$_7$ (1c: a$_2$ = *R*,*R*-dach; 1d: a$_2$ = *S*,*S*-dach): An excess of La(NO$_3$)$_3$·6H$_2$O (2.60 g, 6 mmol) was added dropwise to a solution of [(dach)Pd(2-pymo)]$_4$(NO$_3$)$_4$·*n*H$_2$O (1.76 g, 1 mmol). Slow evaporation at room temperature of the resulting pale yellow solution gave, after two days, a microcrystalline precipitate in nearly quantitative yield. This contrasts with the low yield (ca. 3%) obtained when a similar reaction was performed with [(en)Pd(2-dmpymo)]$_4$(NO$_3$)$_4$·*n*H$_2$O and Gd(NO$_3$)$_3$·6H$_2$O.[23]

{La[(dach)Pd(2-pymo)]$_4$}(NO$_3$)$_7$·*n*H$_2$O (*n* = 10; *R*,*R*: 1c, *S*,*S*: 1d): Elemental analysis (%) calcd for $Pd_4C_{48}H_{96}N_{23}O_{39}La$ (2184.01): C 23.01, H 4.63, N 15.43; found: C 23.03, H 4.38, N 15.25. Yield 80%. ^{1}H NMR (200 MHz, D_2O, 25 °C, TMA): $\delta = 1.01-1.43$ (m, 4H; dach), 1.53–1.75 (m, 2H; dach), 1.89–2.10 (m, 2H; dach), 2.49–2.70 (m, 2H; dach), 6.47 (t, $J_{5,4} = J_{5,4'} = 5.6$ Hz, 1H; H_5), 8.20 (dd, $J_{4,4'} = 2.7$ Hz, 1H; H_4), 8.30 ppm (dd, 1H; $H_{4'}$).

Synthesis of {Na[(dach)Pd(2-pymo)]$_4$}(NO$_3$)$_5$ (1e: *R*,*R*-dach; 1f: *S*,*S*-dach): These compounds were obtained by the methods described above. In this case, the presence of an excess of $NaNO_3$, formed when the pH is raised to 5.5 with 1M NaOH (see synthesis of [a$_2$PdL]$_4$(NO$_3$)$_4$) leads the formation of this type of adducts. These conditions permit the isolation of yellow crystals after four days at room temperature.

{Na[(dach)Pd(2-pymo)]$_4$}(NO$_3$)$_5$·*n*H$_2$O (*n* = 10; *R*,*R*: 1e, *S*,*S*: 1f): Elemental analysis (%) calcd for $Pd_4C_{40}H_{88}N_{21}O_{29}Na$ (1775.93): C 27.05, H 4.99, N 16.56; found: C 26.84, H 4.57, N 16.31. Yield 60%. ^{1}H NMR (200 MHz, D_2O, 25 °C, TMA): $\delta = 1.01-1.43$ (m, 4H; dach), 1.53–1.75 (m, 2H; dach), 1.89–2.10 (m, 2H; dach), 2.49–2.70 (m, 2H; dach), 6.47 (t, $J_{5,4} = J_{5,4'} = 5.6$ Hz, 1H; H_5), 8.20 (dd, $J_{4,4'} = 2.7$ Hz, 1H; H_4), 8.30 ppm (dd, 1H; $H_{4'}$).

Characterisation and physical measurements: Elemental (C, H, N) analyses were obtained on a Fisons-Carlo ERBA EA 1008 analyser at the Centre of Scientific Instrumentation of the University of Granada. IR spectra were recorded on a MIDAC PRS spectrophotometer by using KBr pellets. All ^{1}H NMR spectra were recorded with tetramethylammonium tetrafluoroborate (TMA) as internal reference ($\delta = 3.18$ ppm relative to TMS). 200 MHz ^{1}H NMR spectra were recorded in D_2O with a Bruker AC 200 FT NMR spectrometer. Low-temperature experiments were performed in MeOD. ^{1}H NMR experiments for studying the interaction between metallacalix[*n*]arenes and mononucleotides were performed in D_2O solutions at pH* 6 (pH* denotes uncorrected pH meter readings) with a palladium concentration of 0.033M. These ^{1}H NMR spectra were recorded with a Bruker ARX 400 (400 MHz) (Centre of Scientific Instrumentation of the University of Granada).

X-ray data collection: Intensity data for **1b**, **3b** and **4a** were collected with an Enraf-Nonius KappaCCD diffractometer[26] ($Mo_{K\alpha}$, $\lambda = 0.71069$ Å, graphite monochromator, University of Dortmund). Intensity data for **1f** and **2b** were collected with a Bruker SMART APEX ($Mo_{K\alpha}$, $\lambda = 0.71069$ Å, graphite monochromator, Centre of Scientific Instrumentation of the University of Granada and University of Zaragoza, respectively). Crystal data are listed in Table 1.

In all cases, the whole-sphere reciprocal space was covered by measurements of 360 frames. Preliminary orientation matrices and unit cell parameters were obtained from the peaks of the first ten frames and were refined using the whole data set. Frames were integrated and corrected for Lorentzian and polarization effects by using DENZO.[27] Scaling and the global refinement of crystal parameters were performed by SCALEPACK.[27] Reflections that were partly measured on previous and following frames were used to mutually scale these frames. Merging of redundant reflections partly eliminates absorption effects and, if present, also takes crystal decay into account.

Structure solution and refinement: The crystal structures were solved by standard direct methods[28] and refined by full-matrix least-squares methods on F^2 using the SHELXTL-PLUS[29] and SHELXL-97 pro-

grams.[30] The atom-scattering factors given in the SHELXTL-PLUS program were taken. Transmission factors were calculated with SHEXL-97.[30] All non-hydrogen atoms were refined anisotropically, with the exception of some of the nitrate anions and water molecules. The rather high R value of **1f** may be related to the poor quality of the crystal and the presence of disorder in the uncoordinated sodium cation.

CCDC-209073, CCDC-209074, CCDC-209075, CCDC-209076, CCDC-211043 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

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